

3/PRTS<sup>1</sup>

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COATING MATERIAL

Description

[0001] The present invention relates to conductive nanoparticles with improved properties and transparent coatings made of the same.

[0002] Transparent conductive coatings are of great significance and are well known among other things for displays (CRT, LCD, OLED, ...) and/or antistatic coatings. Standard methods for manufacturing comprise among others first the gas phase coating (sputtering, CVD, PVD, ...) of flat glass with thin, conductive coatings that are transparent in the visible world. Along with (precious) metals, conducting or semi-conducting doped oxides such as ATO ( $\text{SnO}_2\text{:SB}$ ), FTO ( $\text{SnO}_2\text{:Sb}$ ), FTO ( $\text{SnO}_2\text{F}$ ), AZO ( $\text{ZnO:A1}$ ) or ITO ( $\text{In}_2\text{O}_3\text{:Sn}$ ) are used as coating material. As a rule thick coatings are obtained via these methods. This is known as the standard method for the coating of flat glass in order to generate high-quality coatings for flat glass, whereby a fully developed technology is available. The sputter facilities that are used are quite expensive (2 to 3-figure million amounts) and work profitably only in the case of very great operational capacity (coating of several  $100\text{T m}^2/\text{a}$ ). In addition, from a technical standpoint they are very expensive and have a very high material consumption, because when either material that is to be vaporized or a target is vaporized, steam is only partially deposited on the substrate to be coated, while the rest settles somewhere in the interior of the machine. In addition to that, such facilities are inflexible, so that small or special runs are hardly feasible, in particular

since almost exclusively flat geometries can be coated using sputter facilities; other geometries are only possible to a limited extent and the corresponding facility must be rebuilt with each change of geometry. This is somewhat of a problem for automobile glazing, because there are no absolutely flat automobile panes even the attempt to sputter flat panes and then bend them has not succeeded up to this point. Even coating of polymers and films is only possible to a limited extent.

**[0003]** There have also been approaches for realizing such coatings via the use of conductive nanoparticles (e.g. ITO); among others, such methods exhibit as advantages a simple coating technique, e.g. via wet-chemical methods (painting, spraying, pressing, dipping, spin-coating, ...), making possible the direct application of structures, have a low technical expense with correspondingly low investment costs as a consequence, are geometry independent, make better use of the material, have greater flexibility and permit a coating of polymers and films.

**[0004]** However, one basic requirement is the availability of e.g. ITO nanopowder suitable particle size and the redispersibility with the corresponding properties. It is known from US-PS 5,518,810 (Mitsubishi) that a specific shade of color correlates with optimum properties with reference to the infrared shielding; typically blue is an indication of a high number of oxygen defects, thus a high charge carrier density, which is caused by oxygen defects. This is as a rule generated in ITO by annealing the powder or coatings of the powder under inert gas or reducing atmosphere, to be precise in the case of

temperatures above 250° C. This process results in blue powder having a higher conductivity than yellow powder that has not been retreated under reducing atmosphere, and this process results in coatings that have been compressed e.g. by heat treatment at 500° C in the air after inert gas / reducing treatment at temperatures above 250° C show significantly higher conductivities. A subsequent temperature treatment of ITO coatings under reducing / inert atmosphere at temperatures above 250° C is state of the art. However, with many technical applications such a subsequent treatment is often not desirable or not possible, since the coated objects are destroyed at the required temperature, e.g. with CRT or conductive and/or antistatic coatings on plastic. At the same time however the requirements and the need for highly conductive, transparent coatings on plastic are also increasing.

**[0005]** The object of the present invention consists in making something new available for industrial application.

**[0006]** The solution of this task will be claimed in independent form.

**[0007]** Consequently, in accordance with the invention an improvement results in the conductivity of coatings which contain ITO nanoparticles, to be precise with a simultaneous higher transparency in the visible world with a simple coating technique, in particular by means of wet-chemical methods (painting, spraying, pressing, dipping, spin-coating....) with lower technical expenses and lower investment costs.

**[0008]** In the process the better conductivity opens up new fields of application and allows less material (ITO) to be employed for the same conductivity, which leads to more favorable end products. Typically it should be assumed that, when for example coatings are produced, which consist of conductive starting powders and/or in which conductive particles are integrated in a matrix, the conductivity of these coatings will be higher, the higher the conductivity of the starting powders or particles is. However, the invention has recognized that coatings with better conductivity can be produced from yellow powder with actually poorer conductivity than can be produced from blue powder, which as such exhibits a higher conductivity. This will be verified with the help of some typical examples.

**[0009]** Example 1:

Yellow ITO powder is produced in the following manner:

**[0010]** Nanocrystalline  $\text{In}_2\text{O}_3/\text{SnO}_2$  (ITO) powders are produced from an aqueous solution by means of a co-precipitation process in which soluble In or Sn components are precipitated by pH value increase. In this example the concentrations of these compounds were selected in such a way that the Sn concentration amounted to 5 at. % relative to In. However, in principle the Sn concentration can be arbitrarily adjusted.

After separation of the reaction product it is dried and annealed at 300° C under normal atmosphere for 1 hour for the purpose of setting the crystalline phase.

Then the crystalline  $\text{In}_2\text{O}_3/\text{SnO}_2$  is divided into different samples and the individual samples are after-annealed for different periods of time under forming gas at 300 C (see Table 1).

**[0011]** Powders with color indexes that range between the maximum values listed in Table 1 (IT-05 HCB and IT-05 HCG) as well as coatings with yellow indexes between the corresponding values from Table 1 can also be obtained by mixtures of the various powders.

**[0012]** Table 1

Sample name	Duration of treatment	Color index	Yellow index
IT-05 HCB	1.5 hour	x=0.294, y=0.332	0.12
BG9010	1 hour	X=0.301, y=0.341	1.17
BG8515	50 min	X=0.306, y=0.346	2.97
BG8020	45 min	X=0.310, y=0.351	4.63
BG7030	40 min	X=0.318, y=0.361	6.4
BG5050	30 min	X=0.338, y=0.381	12.66
IT-05 GN	1 hour, N <sub>2</sub>	X=0.404, y=0.418	22.7
IT-05 HCG	-----	X=0.414, y=0.421	23.8

**[0013]** Out of yellow ITO powders of to a large extent practically identical particle sizes and with identical dispersion coatings were separated with an organic binder by means of spin-coating and dried at 120° C for 1 hours. The resulting coating thickness and

obtained transparent composite coatings amounted to 3  $\mu\text{m}$ . The conductivity of the coating with blue powder amounted to 1.8 kOhm/square; the conductivity of the coating of yellow powder was 0.8 kOhm/square. The yellow index of both coatings was measured with a color pen (Dr. Lange), evaluated in accordance with DIN 6167 and ASTM D 1925 (standard illuminant C; standard viewer 2°). While the yellow index of the coating of blue powder was below 0.1, the yellow index of the coating made of yellow powder was 23.8.

**[0014]** Example 2:

Out of yellow ITO powders and of blue ITO powders of to a large extent practically identical particle sizes and with identical dispersion transparent coatings were separated by means of spin-coating on the front plate of a kinescope (CRT), to be precise with a coating thickness of 100 nm. After a brief period of drying at room temperature, in order to protect the ITO coating from scratching it was post-coated with a solution of a hydrolysable Si alcoholate by means of spin-coating. The double-coated substrate was heated for 30 minutes at 180° C. After cooling off, the conductivity of the two-coat system is 8.5 k $\Omega$  for the blue powder and 6.1 $\Omega$  for the yellow powder. The surface resistances of the coatings were determined using a 4 point conductivity meter (Loresta GP, Mitsubishi Chemical Corporation).

**[0015]** In the measurements the conductivity of the powders was determined with the arrangement of measuring instruments outlined in Figure 1.

**[0016]** This arrangement of measuring instruments for determination of the conductivity of the powders shows a measuring instrument (multimeter) with reference number 1, a glass pipe with reference number 2, powder with reference number 3, with

reference number 4 an extrusion press ram made of steel and with 5 indicates applied pressure.

**[0017]** The measuring instrument described in Figure 1 was filled with 3.3 g each of powder. Then the upper ram was introduced and contacted with the measuring instrument. The upper ram was then weighted with the various weights and the resulting resistance was measured via the compressed powder charge using a commercial multimeter. The measurements resulted in the following readings:

Weight (kg)	Pressure (kPa)	Resistance (Ohm)	
		Blue powder	Yellow powder
1	77	42	1140
1.5	115	32	820
1.8	138	28	640

**[0018]** The color values of the powders were as follows:

Blue:  $x = 0.294$ ;  $Y = 0.332$

Yellow:  $x = 0.414$ ;  $Y = 0.421$

**[0019]** The characterization of the powders takes place via conductivity and shade of color, the characterization of the coatings takes place via yellow index and conductivity.